Chemosystematic Notes on the Asteraceae II
Acyclic Sesquiterpenes

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Abstract

Elaborated acyclic sesquiterpenes prove taxonomically significant in the Eupatorieae and Anthemideae. Distinctive forms occur in each tribe and a unique type of ester occurs in Brickellia. *Presence of Furansesquiterpenes correlated with lack of polyacetylenes further demonstrates the position of* Ursinia *in the Anthemideae.*

The acyclic sesquiterpenes in their simpler forms occur widely, Farnesol (1) as an example being found in the essential oils of many plant families. The compounds are widely distributed in members of the Asteraceae usually representing the simple precursor of the numerous sesquiterpene, diterpene and triterpene chemical pathways developed in that family. In the recent Symposium on the Biology and Chemistry of the Compositae only the treatment on the chemistry of the Anthemideae by Greger (1977) gave the chemical group any but casual notice. It seems that a few points should be brought out more clearly and the status of the group in the Asteraceae should be summarized.

The acyclic sesquiterpenes are potentially the simplest of the sesquiterpene compounds and should exist as intermediates in all sesquiterpene, pathways even though they may not accumulate in detectable amounts. Unelaborated forms such as Farnesol (1) are close in form to the basic theoretical three-isoprene unit of all sesquiterpenes. The general structure of the acyclics can be shown in a variety of ways, many of which suggest the manner in which they can form rings leading to other sesquiterpene types.

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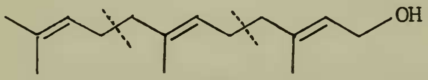

Farnesol

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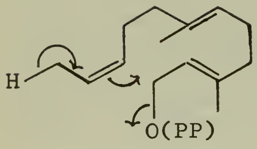
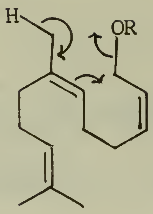
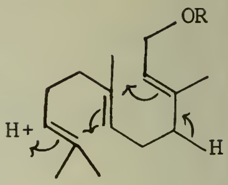


2. Germacradiene



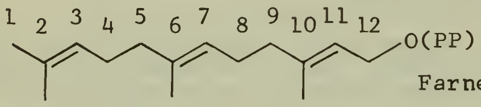
3. Bisabolene



4. Drimenol

The general representation preferred here is the linear form of the carbon skeleton as represented by farnesol pyrophosphate (5) the general precursor of other forms of acyclic sesquiterpenes in the Asteraceae.

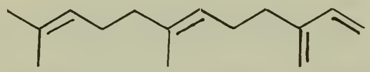
5.



Farnesol pyrophosphate (E, E)

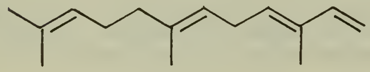
This compound is presumed to occur in all tribes of the family in which other sesquiterpenes are found. Simple modifications involving elimination of water (6, 7) are also widely distributed in the family.

6.



β-farnesene

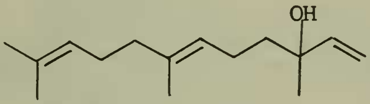
7.



α-farnesene

In the tribes the Eupatorieae and Anthemideae the acyclic sesquiterpenes become elaborated and these elaborations are characteristic of the tribes. In a few cases the elaborations are characteristic of genera or groups of genera. One specialized feature found in both tribes is the use of the precursor (8) nerolidol with a tertiary alcohol group at C-10.

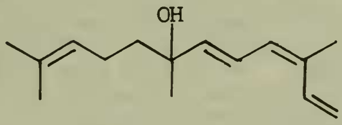
8.



This has also been seen in one species of *Pentacalia* in the Senecioneae. In spite of the occurrence of the tertiary alcohol in both tribes, other specializations in the compounds result in none of these derived forms of acyclics being precisely alike in both tribes.

In the Eupatorieae other specializations occur in various members of the tribe which do not occur in the Anthemideae. In *Ageratina, Brickellia, Eupatorium, Eupatoriadelphus* and *Peteravenia* there are tertiary alcohols formed by introduction of an O-function at C-6 by allylic rearrangement starting with (7). Examples are 9 and 10.

9.



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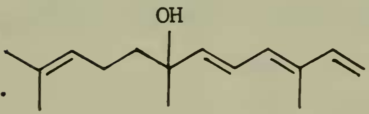
Eupatorium perfoliatum L.

Brickellia californica A.Gray

↙

10.



←

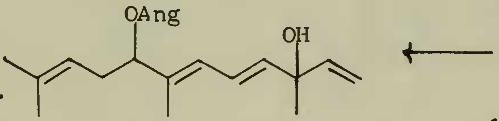
Ageratina bustamenta (DC.) K. & R.

Brickellia laciniata A.Gray

One of the examples shows an additional specialization, the altered stereoisomerism of the 9,10-double bond (9). At least two basic phyletic lines in the Eupatorieae are represented by each of these specializations and they are regarded as markers at the tribal level only.

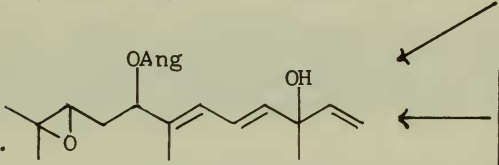
Within the Eupatorieae the most phyletically significant elaboration seems to be the further transformation of nerolidol (8) to 5-hydroxydehydro nerolidol and esterification with Angelic acid. This specialization is found only in the genus *Brickellia* where it is seen in five species (11, 12).

11.



B. argyrolepis B.L.Robins.
B. cylindrica A.Gray & Engelm.
B. guatemalensis B.L.Robins.

12.

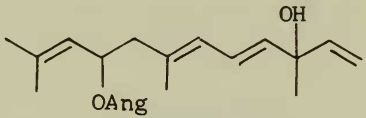


B. pacayensis Coulter
B. squarrosa B.L.Robins. & Seaton

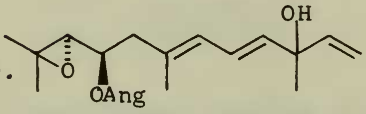
A genus related to *Brickellia, Pseudokyrsteniopsis,* has been examined but no acyclic sesquiterpenes have been found.

Introduction of an angeloyloxy group at C-4 is common in the tribe, found in 8 genera, in potentially 6 subtribes, but it has been found in only one *Brickellia*. The simpler form (13) is known from *Brickellia vernonicaefolia* A. Gray, *Eupatoriadelphus dubius* (Willd. ex Poir.) K & R., *Eupatorium hyssopifolium* L., and *Radlkoferotoma cistifolium* (Less.) O. Kuntze. The derived forms with the ester can be divided techically into two groups depending on the stereoisomerism derived from the oxidation at C-2 and 3.

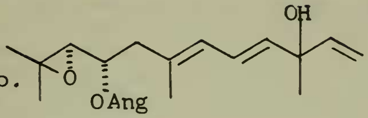
13.



14a.



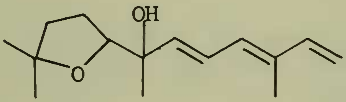
14b.



The stereoisomer 14a is found in *Bishovia, Eupatorium, Eupatoriadelphus, Heterocondylus* and *Peteravenia.* Stereoisomer 14b is found only in *Ageratina scorodonoides* (A. Gray) K. & R. and *Hebeclinium macrophyllum* (L.) DC. The two genera containing 14b are not in the same subtribe and the last is actually closer in relation to *Peteravenia* than to *Ageratina.*

The epoxidation of the carbon 2-3 bond occurs in numerous members of the Eupatorieae with ester formation at C-4 but it also occurs in most acyclics of the five *Brickellia* species with ester formation at C-5. This precise form of oxidation is not found in the absence of the Angelic acid esters. Still, an interesting variant occurs in *Ageratina bustamenta* (DC) K. & R. (15) which indicates the form that oxidation would take in the absence of the ester side chains.

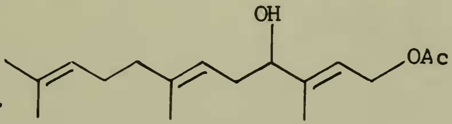
15.

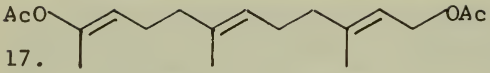


The acyclic sesquiterpenes of the Anthemideae also are elaborated by oxidation and esterification, but the esters are acetates and the oxygen is often in the form of ketones or furans. There is also an example of alcohol formation in a secondary position at C-9 instead of C-10 (16).

The acetates may form at C-12 or on both ends of the molecule or at C-5 or C-8 (16, 17, 18) (Bohlmann, et al, 1974).

16.





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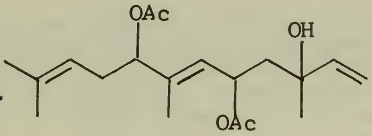
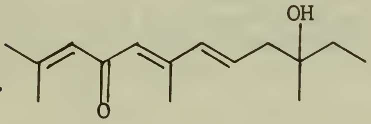


18.

All in *Tanacetum*

Ketone formation at C-4 is found in comparatively simple acyclics in *Anthemis austriaca* (19, 20) (Bohlmann, et al, 1974) but is not known in *Tanacetum*.



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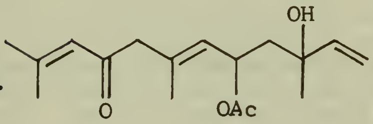
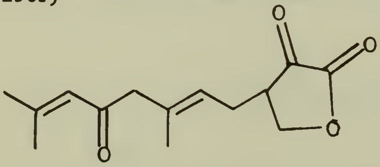


20.

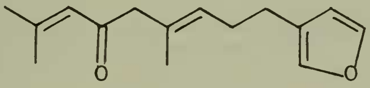
The ketone unit is also present in combination with a highly modified oxidized end unit in *Anthemis cotula* (21) (Bohlmann, et al, 1969)



21.

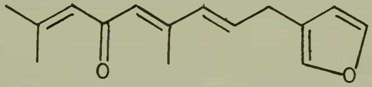
Furanosesquiterpenes occur in a distinctive series of South African genera of the Anthemideae, *Asaemia*, (1 sp. examined) *Athanasia*, (13 sp.) *Eumorphia*, (2 sp.) *Lasiospermum*, (4 sp.) *Phymaspermum*, (2 sp.) *Stilpnophytum*, (1 sp.) and *Ursinia*, (5 sp.). There are 35 different types of these compounds known. The following are examples taken from Greger (1977).

22.



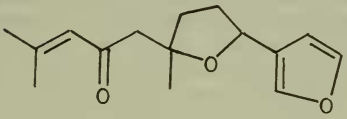
In *Athanasia*, *Lasiospermum* and *Stilpnophytum*

23.



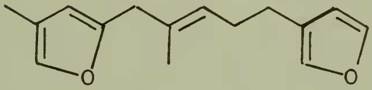
In *Phymaspermum*

24.



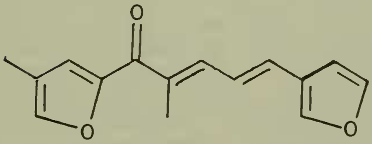
In *Athanasia* and *Lasiospermum*

25.



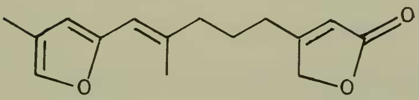
In *Athanasia* and *Asaemia*

26.



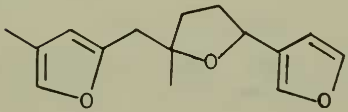
In *Athanasia*, *Asaemia* and *Eumorphia*

27.



In *Athanasia*

28.



In *Athanasia* and *Eumorphia*

The occurrence of Furanosesquiterpenes in this distinctive group of genera correlates with an absence of Polyacetylenes that is unusual in the Anthemideae. The exact relationship of the group to the Anthemideae has been questioned (Heywood & Humphries, 1977) and *Ursinia* has been placed in the far removed Arctotideae in the traditional systems of Bentham and Hooker (1873) and Hoffmann (1890-1894). The erroneous positioning was the result of the geographical and pappus similarity between *Ursinia* and *Arctotis*. Corrections of the position of *Ursinia* and placement in or near the Anthemideae (Beauvard, 1915; Prassler, 1967; Robinson & Brettell, 1973) have relied on structural considerations. The correlation of Furanosesquiterpene presence and Polyacetylene absence provides confirmation of the relationship of *Ursinia* at least to the distinctive series of genera in South Africa that have been consistently included in the Anthemideae.

The further position of the *Athanasia-Ursinia* group in the Anthemideae seems to be confirmed in three ways by the Furanosesquiterpenes. Initially, elaborated acyclic sesquiterpenes are known only from the two tribes Eupatorieae and Anthemideae. Secondarily, the ketone formation at C-4 seen in *Anthemis* is also seen in some of the most widely distributed Furanosesquiterpenes, though ketone units at C-5 are seen also. A final and more tenuous link is in the presence of the furan units. Though polyacetylenes are absent when Furanosesquiterpenes are present, the furan units are reminiscent of furan units in Polyacetylenes of other members of the Anthemideae. The general picture from an over-view of Polyacetylenes in the Asteraceae shows a tendency for highly oxygenated products in the Anthemideae in comparison to some other tribes such as the Heliantheae and Eupatorieae. It seems significant that the acyclic sesquiterpenes of the tribe would show the same tendency for highly oxygenated products. It is suggested that the same enzymatic pathways are operating in the elaboration of both Acyclic sesquiterpenes and Polyacetylenes in the Anthemideae, and that these pathways are not evident in either group of chemicals in the Eupatorieae or in the Polyacetylenes of most tribes of the Asteraceae.

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